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(54) **Process for upgrading petroleum fractions containing olefins and aromatics**

(57) A petroleum fraction, for example catalytic gasoline, containing aromatics and olefins, is upgraded by contacting the fraction with a solid catalyst under con-

ditions to alkylate aromatics in the fraction with olefins in the fraction. The process reduces the olefin content and decreases the octane number sensitivity of the fraction. Benzene content may also be reduced.

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Description

BACKGROUND

Alkylation of aromatics produced from reformers has been practiced commercially. Recent technology for reduction of benzene content reacts C_2 to C_4 olefins with benzene to produce C_8 to C_{10} aromatics. Such processes react aromatics from reformer operations with light hydrocarbon olefins from refinery gas plant operations, the source of the olefins being the catalytic cracking unit. With the passing of the 1990 Clean Air Act, all components going to the gasoline pool will be under scrutiny for their performance, quality and toxicity.

Using light hydrocarbon olefins from another refinery stream to alkylate aromatics in catalytic gasoline has the disadvantage that the light hydrocarbon olefins have other potential uses in which they may be more valuable. Thus, for example, they make excellent petrochemical feedstocks, gasoline component reactants and commodity chemicals. Ethylene and propylene components of light hydrocarbon olefins are used as reactants in the manufacture of plastics. Refineries alkylate propylene and butylene components of light hydrocarbon olefins with alkanes to produce gasoline components with good octane for their gasoline pools. Reacting light hydrocarbon olefins with benzene to reduce the pool benzene content may be a downgrade of the olefins and a cost-ineffective operation for the refiner.

The octane number of gasoline as marketed is expressed as road octane number, which is calculated as the numerical average, $(R+M)/2$, of Research Octane Number (RON) and Motor Octane Number (MON). Refiners usually need to satisfy both a road and an MON octane minimum for their gasoline grades.

The olefins normally contained in catalytic gasoline contribute good octane numbers to the catalytic gasoline. However they have the highest octane number sensitivity, which is the difference between RON and MON. Therefore to meet an MON specification for the gasoline, a highly olefinic gasoline may have excessive RON. This yields a road octane in excess of the minimum, resulting in octane giveaway. Having the means to control MON and road octane numbers separately gives the refiner flexibility to produce a more consistent octane pool.

Reducing olefin content reduces the sensitivity and the octane giveaway. Another benefit from reducing olefin content is that olefins are significant contributors to the vapor pressure of the gasoline blend. Reducing olefin content reduces the vapor pressure of gasoline and gives the refiner blending flexibility by enabling the refiner to blend gasoline with desirable higher vapor pressure components without exceeding the maximum desired vapor pressure for the blend.

Solid superacids have been disclosed for catalyzing alkylation of aromatics with olefins. Solid superacids comprising sulfated and calcined oxides or hydroxides of Group III or IV, Group V, VI or VII and Group VIII metals have been disclosed for such purpose in E.J. Hollstein, J.T. Wei and C-Y. Hsu U.S. Patents 4,918,041, April 17, 1990; and 4,956,519, September 11, 1990.

The alkylation of light aromatics in a refinery stream containing a minor amount of benzene with olefins in a separate olefin-containing refinery stream, and using for example a beta zeolite in its hydrogen form as catalyst for the alkylation, is disclosed in C.R. Hsieh et al U.S. Patent 5,082,990 issued January 21, 1992 from an application filed November 1, 1990. The benzene-containing stream may be a reformate stream, and the olefin-containing stream may be fluid catalytic cracking off-gas containing hydrogen, C_1 to C_3 alkanes, and C_2 and C_3 olefins.

Solid superacids comprising Group IV-A metals and two or more additional metals have been disclosed for catalysis of alkanes with olefins in H.P. Angstadt, E.J. Hollstein and C-Y. Hsu U.S. Patents 5,212,136, May 18, 1993 and 5,214,017, May 25, 1993.

DESCRIPTION OF THE INVENTION

The process of the invention upgrades a petroleum fraction containing olefins and aromatics by contacting the fraction with a solid catalyst under conditions to alkylate aromatics in the fraction with olefins in the fraction, to reduce the olefin content and decrease the octane number sensitivity of the fraction. In one embodiment of the invention, the benzene content of the fraction is also reduced, by alkylation of the benzene to higher aromatics.

FEEDSTOCK

The feedstock for the process of the invention comprises a petroleum fraction containing olefins and aromatics. Preferably, the feedstock is at least partly in the gasoline boiling range. The gasoline treated may be either individual gasoline stocks prior to blending or blended gasoline containing two or more individual gasoline stocks. Preferably the gasoline treated according to the invention contains about 3 to about 40 weight percent olefins and about 10 to about 50 weight percent aromatics, more preferably about 10 to about 35 weight percent olefins and about 20 to about 45 weight percent aromatics.

A typical gasoline for treatment according to the invention may contain 20-25 wt% paraffins, 20-30 wt% olefins, 5-15 wt% naphthenes and 35-40 wt% aromatics. However, any feedstock containing substantial amounts of olefins

and aromatics may be employed in the invention. The olefins in the feedstock typically comprise C_4 to C_{13} olefins, and the aromatics in the feedstock C_6 to C_{12} aromatics. Examples of feedstocks suitable for treating by the process of the invention are catalytically cracked gasoline, coked gasoline and the like.

5 CATALYST

Any of the known solid alkylation catalysts may be used in the process of the invention. Examples are the well-known solid phosphoric acid alkylation catalysts, zeolite alkylation catalysts and solid superacid alkylation catalysts. Other solid alkylation catalysts as known in the art may be employed. Solid superacids are preferred catalysts for use according to the invention.

PROCESS CONDITIONS

The conditions used in the process of the invention are those at which alkylation of aromatics in the fraction with olefins in the fraction take place. The process of the invention is preferably carried out at temperatures in the range from about 50 to about 150°C and pressures in the range from about 250 to about 450 pounds per square inch gauge. However, any conditions capable of resulting in substantial alkylation of aromatics with olefins may be employed. The alkylation of aromatics with olefins results in a decrease in weight percent of olefins in the fraction. An increase in weight percent of aromatics in the fraction also occurs because of the higher molecular weight of the aromatic alkylation products.

SOLID SUPERACID CATALYSTS

The process of the invention preferably uses solid superacid catalysts to catalyze the alkylation of aromatics with olefins. The solid superacid catalysts which have been disclosed in the prior art for use as alkylation catalysts are generally suitable for use according to the invention. Preferred solid superacid catalysts for use according to the invention are the solid acids which have acidities stronger than 100% H_2SO_4 (i.e. $H_0 < -12$). Examples of the solid superacids are sulfated zirconia, sulfated titania, sulfated iron oxide, sulfated zirconia containing one or more metals, sulfated titania containing one or more metals, halogenated alumina such as fluorinated Al_2O_3 , etc., titania zirconia mixtures calcined at 800°C, etc. Other types of solid superacids are strong Lewis acids such as SbF_5 , $SbCl_5$, SbF_5/HF , on a solid support such as silica, alumina or zirconia or combinations thereof.

Solid superacids which can be used in the process of the invention include sulfated and calcined solid oxides or hydroxides of Group III and/or IV metals, which may also comprise sulfated and calcined oxides and/or hydroxides of Group V, VI, VII and/or VIII metals.

Group III and IV metals in solid superacids useful in the process of the invention include aluminum, gallium, indium, thallium, titanium, zirconium, hafnium, silicon, germanium, tin and lead. Preferred are silicon, aluminum, zirconium, titanium and mixtures of two or more thereof.

Group V, VI and VII metals in solid superacids useful in the process of the invention include arsenic, antimony, bismuth, vanadium, niobium, tantalum, selenium, tellurium, chromium, molybdenum, tungsten, manganese and rhodium and mixtures of two or more thereof.

Group VIII metals in solid superacids useful in the process of the invention include iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium and platinum and mixtures of two or more thereof.

The catalysts used according to the invention may comprise sulfated and calcined oxides or hydroxides of Group III or IV elements, for example zirconium, and Group VIII, first row elements, for example iron, and/or Group VIII third row elements, for example platinum.

The catalysts used according to the invention may be prepared for example by impregnating a support of a Group III or IV metal oxide or hydroxide, for example zirconia, with an aqueous solution of a compound of a Group VIII metal, for example iron. The solution may contain compounds of more than one metal, or the support may be impregnated with a series of two or more solutions containing different metals.

The catalysts used according to the invention may also be prepared by coprecipitation of solid hydroxides of a Group III or IV metal and one or more additional metals, from aqueous solutions containing compounds of such metals. The additional metals may be from Group I-B, II-B, III-A, III-B, IV-B, V-A or VI-A, and/or from the Lanthanide Series of the Periodic Table. Such catalysts are disclosed for example in H.P. Angstadt, E.J. Hollstein, C-Y. Hsu U.S. Patents, 5,212,136 and 5,214,017 supra.

Solutions of metal compounds which can be used in the preparation of solid superacid catalysts for use according to the invention, by impregnation or coprecipitation, are known in the art. Solutions of zirconium oxychloride or of zirconyl nitrate can be used for example to prepare a zirconium support for the catalyst according to the invention. For example, aqueous solutions of chloroplatinic acid or tetra-ammine-platinum complex can be used to incorporate plat-

in the catalyst. Nitrates of metals, for example iron, can be used for example to incorporate those metals in the catalyst. Various other solutions can be employed as needed.

Sulfate ion may be supplied to the catalyst according to the invention by treatment of the solid catalyst with sulfuric acid, for example 0.01-10 N sulfuric acid, preferably 0.1-5 N sulfuric acid. Other compounds such as ammonium sulfate capable of providing sulfate ion can be employed. Compounds such as hydrogen sulfide or sulfur dioxide or mercaptans, capable of forming sulfate ions upon calcining, can also be employed.

A sulfated zirconia catalyst containing platinum, iron and manganese may be prepared for example by the following procedure: Zirconyl nitrate (462.46 grams), ferric nitrate (26.74 grams) and manganese nitrate (5.62 grams) are dissolved in de-ionized water to make 1 liter of solution A. 260 grams of concentrated ammonium hydroxide are diluted with sufficient de-ionized water to make 1 liter of solution B. 500 ml of de-ionized water are added to a 5 liter Morton flask. Solution A and Solution B are added concurrently through two addition funnels to the Morton flask slowly with rapid stirring. The temperature of the precipitation reaction is maintained at about 65°C. The pH of the resulting mixture is maintained at about 7.0. The reaction slurry is filtered and the filter cake washed with de-ionized water several times until the filtrate is nitrate-free. The damp cake is applied to perforated plates, placed in a tray and dried overnight at 150°C. The dried pellets are added slowly to a beaker containing 1.0 N sulfuric acid solution at room temperature. The amount of sulfuric acid is determined by the ratio of 15 ml of 1.0 N sulfuric acid per gram of pellet. The sulfuric acid solution is decanted after the pellets have been soaked for two hours. The pellets are then calcined at 725°C for one hour. The iron and manganese concentrations in the final catalyst are 1.5% and 0.5% respectively (Preparation I). The pellets from Preparation I (20-40 mesh) are impregnated with an aqueous solution (incipient wetness) of chloroplatinic acid. The preparation is dried overnight at 120°C. and then calcined at 450°C. for 16 hours. Such procedure may produce for example a catalyst containing 0.25% Pt on 1.5% Fe, 0.5% Mn and 4.0% SO_4 impregnated ZrO_2 .

Catalysts containing sulfated and calcined oxides or hydroxides of Group VIII elements and Group III or IV elements can be prepared for example by impregnating Group VIII metals, for example nickel, platinum, ruthenium, rhodium, palladium, osmium or iridium, and sulfate ion or precursor thereof, in a carrier made of hydroxide of Group IV metals, for example titanium, zirconium, hafnium, silicon, germanium or tin, and/or hydroxide of Group III metals, for example aluminum, gallium, indium or thallium, and stabilizing by roasting at 450-800°C for 5 to 16 hours.

MOLECULAR SIEVE / ZEOLITE CATALYST

Catalysts which may also be used in the process of the invention are the molecular sieve and zeolite alkylation catalysts. Examples of such catalysts include shape-selective zeolite such as ZSM-5, ZSM-12 mordenite, beta zeolite, hydrogen or rare-earth exchanged zeolite, SAPO-11, SAPO-37, Y-82, LZ-20, and LZ-210 zeolites and the like. Y-82, LZ 20 and LZ-210 are brand names of zeolites which are isostructural with faujasites and have different Si/Al ratios created by ion exchange and steaming and/or by secondary synthesis methods. The pure molecular sieve or zeolite may be used as a catalyst, but generally it is preferred to mix the molecular sieve or zeolite powder with an organic oxide binder such as alumina, silica, silica/alumina, or naturally occurring clays and form the mixture into tablets or extrudates. The final catalyst may contain from 1 to 99 weight percent zeolite. Usually, the molecular sieve or zeolite content will range from 10 to 90 weight, and more typically from 60 to 80 weight percent. The preferred inorganic binder is alumina. The mixture may be formed into tablets or extrudates having the desired shape by methods well known in the art. The extrudates or tablets will usually be cylindrical in shape. Other shapes with enhanced surface-to-volume ratios, such as fluted or poly-lobed cylinders, can be employed to enhance mass transfer rates and, thus, catalytic activity.

ADVANTAGES OF THE PROCESS OF THE INVENTION

Alkylation of catalytic gasoline aromatics with catalytic gasoline olefins offers the refiner new opportunities. By using olefins in the gasoline, rather than the light olefins which have heretofore been used for alkylation of aromatics in catalytic gasoline, the process of the invention frees up the light olefins for chemical sales and alkylation. The process of the invention also reduces the olefin content of the catalytic gasoline for improved blending flexibility.

In the process of the invention, aromatics in catalytic gasoline are alkylated with the olefins in catalytic gasoline. The octane sensitivity is thereby reduced, octane giveaway reduced, and vapor pressure reduced. Benzene content is typically not increased and may be reduced.

The process of the invention comprises treating catalytic gasoline in a unit where the catalytic gasoline is contacted at alkylation conditions with solid superacid catalyst. The treatment is preferably but not necessarily carried out before gasoline blending. At conditions normally found for catalytic gasoline recovery the solid superacid catalyst alkylates the aromatics with olefins in the gasoline. The process may be a simple add-on to a gasoline recovery train and not require a unit shutdown to commission.

EXAMPLES

Catalytic gasoline was treated with alkylation catalyst to alkylate olefins in the catalytic gasoline with aromatics in the catalytic gasoline. The catalytic gasoline had composition and octane number properties as shown in column A of Table 1. In Runs 1 and 2, the catalytic gasoline was contacted with a solid superacid catalyst comprising sulfated (4.0% SO₄) and calcined iron (1.5%) and manganese (0.5%) oxides on zirconia, at the conditions shown at the head of Columns 1 and 2 of Table 1. Thus, in Run 1, the catalytic gasoline was contacted with the catalyst at 75°C and 335 psi of N₂ pressure.

In Runs 3, 4 and 5, the catalytic gasoline was contacted with a solid superacid catalyst comprising sulfated (4.0% SO₄) and calcined platinum (0.025%), iron (1.5%) and manganese (0.5%) on zirconia, at the conditions shown at the heads of Columns, 3, 4 and 5 of Table 1.

The compositions and the octane number properties of the products of Runs 1 through 5 are shown in Table 1 for each of the five runs.

The data in Table 1 show that in all cases the treatment according to the invention reduced olefin content and raised aromatic content. In most cases, namely Runs 1, 2, 3 and 4, the benzene content appears slightly reduced. In all cases the MON number was equal to or greater than that of the feedstock. In all cases, the octane number sensitivity (RON-MON) of the product (10.5, 10.3, 10.6, 10.6 and 8.5 for Runs 1 through 5) was less than that of the feedstock (10.9). These shifts were accomplished without any external feed of olefin to the process.

	Run #	1	2	3	4	5
	Catalyst	Fe/Mn	Fe/Mn	Pt	Pt	Pt
	Temperature	75°C	75°C	75°C	75°C	100°C
	Pressure	335 N ₂ psi	345 H ₂ psi	320 N ₂ psi	310 H ₂ psi	500 H ₂ psi
Composition:						
wt% Paraffins	22.3	21.6	21.7	21.3	21.7	27.0
wt% Olefins	25.9	21.5	21.7	23.1	23.6	11.4
wt% Naphthenes	10.6	10.0	10.6	10.4	10.8	10.8
wt% Aromatics	38.3	42.3	41.0	40.3	40.3	43.6
wt% >200°C	2.9	4.6	5.0	4.9	3.6	7.2
Aromatics:						
Benzene	0.79	0.76	0.78	0.74	0.77	0.79
C ₇ to C ₁₀	34.2	35.5	34.5	34.6	34.9	32.7
C ₁₁ +	3.3	6.0	5.7	5.0	4.6	10.1
Olefins:						
C ₅ to C ₇ iso	11.1	8.8	8.1	8.7	9.3	3.9
C ₅ to C ₇ linear	6.2	5.6	5.6	5.6	5.6	2.5
Paraffins:						
iso/linear ratio	4.8	5.0	4.7	4.7	4.6	3.0
Octanes Determined by Composition:						
RON	92.8	92.7	92.3	92.5	92.5	90.6
MON	81.9	82.2	82.0	81.9	81.9	92.1
R+M/2	87.4	87.45	87.15	87.2	87.2	86.35
Change	0	+0.05	-0.25	-0.2	-0.2	-1.05

Claims

1. Process for upgrading a normally liquid petroleum fraction containing olefins and aromatics which comprises contacting said fraction with a solid alkylation catalyst under conditions to alkylate at least some of said aromatics with at least some of said olefins, thereby to reduce the olefin content and decrease the octane number sensitivity of said fraction.
2. Process according to claim 1, wherein said conditions comprise temperatures in the range from about 50° to about 150°C and pressures in the range from about 250 to about 450 pounds per square inch gauge.
3. Process according to claim 1 or 2, wherein said catalyst comprises solid superacid.
4. Process according to any of claims 1 to 3, wherein said catalyst comprises sulfated and calcined Group III or Group IV metal oxide or hydroxide.
5. Process according to any of claims 1 to 4, wherein said catalyst comprises one or more Group VIII metal oxides or hydroxides, preferably oxides or hydroxides of iron or platinum.
6. Process according to any of claims 1 to 5, wherein said catalyst comprises one or more Group VII metal oxides or hydroxides, preferably oxides or hydroxides of manganese.
7. Process according to any of claims 1 to 6, wherein said catalyst comprises platinum, iron and manganese oxides or hydroxides.
8. Process according to any of claims 1 to 7, wherein said fraction is catalytically cracked gasoline, preferably containing about 3 to about 40 weight percent olefins and about 10 to about 50 weight percent aromatics, more preferably about 10 to about 35 weight percent olefins and about 20 to about 45 weight percent aromatics.
9. Process according to any of claims 1 to 8, wherein said catalyst comprises a zeolite or molecular sieve.
10. Process according to any of claims 1 to 9, wherein said catalyst further comprises an inorganic binder, wherein said binder is preferably selected from the group consisting of alumina, silica, alumina/silica, and naturally-occurring clays, and most preferably comprises alumina.